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FIRST QUARTERLY LETTER REPORT

THERMODYNAMIC PROPERTIES OF PROPELLANT
COMBUSTION PRODUCTS

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Code 1

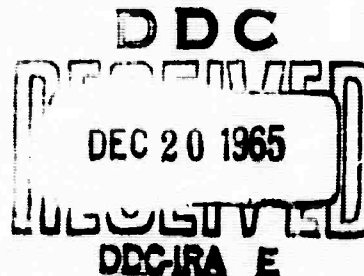Contract AF 49(638)-1577, Dated 1 June 1965

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## Introduction

The objective of this program is to provide thermodynamic data for species which are potentially important combustion products of advanced chemical rockets and for species which are related to these. Enthalpy and entropy data are obtained from equilibrium measurements made by torsion-free evaporation and torsion-effusion techniques and by high temperature mass spectrometry.

## Group IIIB Halides

In measuring the bond dissociation energy of BF[1] it was found that thermochemical results gave a value which was 5 Kcal/mole lower than the results derived from spectroscopic studies of the emission spectrum of BF.[2] Since this discrepancy seemed real, and since AlF showed a similar discrepancy between thermochemical and spectroscopic determinations of $D_0^0(AlF)$, it was decided to determine the dissociation energy of other group IIIA monofluorides. The results on GaF have been presented before.[3] The following equilibrium involving InF has been studied mass spectrometrically in the system In + $CaF_2$:

$$In(g) + CaF(g) = InF(g) + Ca(g) \qquad (1)$$

The appearance potentials of these species were: $In^+$ = 5.8 eV, $InF^+$ = 9.6 eV, $Ca^+$ = 6.0 eV, and $CaF$ = 6.0 eV.

Ion intensities for these species were measured 5 eV above threshold in the temperature range $1561^0$ to $1693^0$ K. and the results are given in Table I. The free-energy function of InF were calculated from the spectroscopic data of Barrow, et al.[4] Functions for other species were taken from available compilations. Third-law calculations gave $\Delta H_{298}$ (1) = +5.2 $\pm$ 0.9 Kcal/mole, which yielded upon use of known heats of formation $D_0^0$ (InF) = 121 Kcal/mole.

In addition to the work on InF a brief study of the system Tl + $MgF_2$ was made, the purpose being to determine the heat of formation of TlF. The following equilibrium was studied:

$$Tl(g) + MgF(g) = TlF(g) + Mg(g) \qquad (2)$$
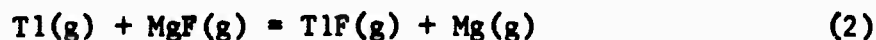
The appearance potentials of these species were: $Tl^+$ = 6.4 eV, $TlF^+$ = 12 eV, $Mg^+$ = 7.6 eV, and $MgF^+$ = 7.6 eV. The ion intensities were measured approximately 5 eV above threshold in the temperature range $1546^0$ to $1585^0$K. The results are given in Table II. The free-energy function of TlF were calculated from the spectroscopic data of Barrow et al.[5] Third-law calculations gave $\Delta H_{298}$(2) = +5.5 $\pm$ 0.5 Kcal/mole, which yielded upon use of known heats of formation $D_0^0$ (TlF) = 101.4 Kcal/mole.

The results of these studies are summarized in Table III. It should be

noted that $D_o''$ derived from spectroscopic studies are always higher than those derived from thermodynamic equilibrium results. It is worth noting that the difference between the spectroscopic and thermochemical studies is less than the previously given value of 11 Kcal.[2,6] The new difference of 8 Kcal results from a redetermination of $\Delta Hf^o_{298}\left[AlF_3(c)\right]$[7] which is used in a cycle to determine $\Delta Hf^o_{298}\left[AlF(3)\right]$.

Since the spectroscopic values are obtained from an extrapolation of the first excited $^1\Pi$ state of these molecules, it is reasonable to attribute the difference between the spectroscopic studies and the thermochemical studies to the existence of a potential maximum in the $^1\Pi$ state. Indeed, Barrow had concluded that such a maximum exists for AlF.[2,6] A paper is being written on this subject and will soon be submitted for publication in the Journal of Molecular Spectroscopy.

## Heat of Sublimation of Aluminum

Torsion-effusion cells, constructed of beryllia, are being used to measure the vapor pressure of aluminum. In our first several runs, a granular aluminum sample (stated minimum purity 99.99%) was used and the data yielded a heat of sublimation, $\Delta H_{298} = 80.3 \pm 0.4$ Kcal/mole by third-law analysis. Measurements were then made on samples cut from a high purity aluminum rod. Four runs on this sample yielded a heat of sublimation of $80.0 \pm 0.2$, $80.0 \pm 0.2$, $80.2 \pm 0.3$ and $80.6 \pm 0.4$ Kcal/mole, respectively. After these runs, the sample surface appeared grey. It is believed that the sample became coated with an oxide film in the last experiments and was also covered somewhat in the original experiments where the granular aluminum sample was used.

Measurements of the decomposition pressure of aluminum carbide can also be used to derive the heat of sublimation of aluminum. It has been shown[8,9] that aluminum carbide in a graphite cell decomposes as

$$1/4\ Al_4C_3(c) = Al(g) + 3/4\ C(c) \tag{3}$$
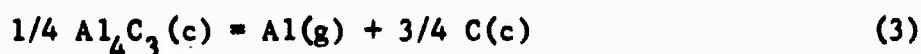
Since there is a reasonably firm value for the heat of formation of aluminum carbide[10,11,12] the heat of sublimation of aluminum can be derived from the heat of reaction three. From a series of preliminary torsion-effusion measurements, in which it was found there is a small hole-size effect, the heat of reaction three was found to be $\Delta H_{298} = 95.1 \pm 2.0$ Kcal/mole. This is to be compared with a value, $\Delta H_{298} = 93.2$ Kcal/mole found by Meschi and Searcy.[9] These heats of reaction lead to heats of sublimation for aluminum $\Delta H_{298} = 82.3 \pm 2.5$ and $\Delta H_{298} = 80.4$ Kcal/mole, respectively.

It would seem then that the accepted heat of sublimation of aluminum, 76.8 Kcal/mole, may be too low. Further work is underway, both with the vaporization

of metallic aluminum from beryllia cells and with the decomposition reaction of
aluminum carbide, to better determine the heat of sublimation of aluminum.

## Beam Modulation

The relevant parts of the mass spectrometer have been sent to the shop and
the new chopper wheel, flexible drive and externally mounted motor are being
installed. It is expected that the beam modulation apparatus will be tested and
in operation during the next quarter.

## Major Accomplishments

New data on the heat of formation of the group IIIA monofluorides have
been obtained, preliminary measurements have been carried out on the heat of subli-
mation of aluminum and work has continued on modification to the mass spectrometer.
This last will greatly increase the usefulness of the instrument for our studies.

## Problems Encountered

No major technical problems were encountered.

## Future Plans

The work on the mass spectrometer modifications will continue. Some
additional work will be done on this group IIIA monofluorides and further work will
be done to measure vapor molecular weights by combined torsion-effusion and effusion-
weight loss measurements.

## Action Required of Government

None.

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10. Alla D. Mah, U.S. Bureau of Mines, Rept. on Investigation 6415, 1964.

11. C. S. Campbell, Met. Soc. Conf. $\underline{7}$, 412 (1962).

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## Table I

### Ion Intensities, Equilibrium Constants and Third-Law
### Heats for the Reaction

$$In(g) + CaF(g) = InF(g) + Ca(g) \qquad (1)$$
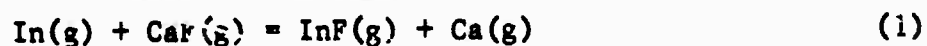
| $T(^oK)$ | $I(In^+)$ 11 V. | $I(InF^+)$ 15 V. | $I(Ca^+)$ 11 V. | $I(CaF^+)$ 11 V. | $K_1$ | $\Delta H_{298}(1)$ Kcal/mole |
|---|---|---|---|---|---|---|
| 1593 | 101.5 | 10 | 9 | 29.5 | 0.038 | +4.8 |
| 1595 | 23.5 | 2.4 | 4.8 | 13.5 | 0.036 | +5.1 |
| 1618 | 35 | 2.1 | 6.2 | 14.5 | 0.025 | +6.3 |
| 1624 | 13.8 | 1.2 | 5.0 | 18.1 | 0.024 | +6.5 |
| 1625 | 110 | 12.5 | 9 | 29.5 | 0.035 | +5.4 |
| 1641 | 39 | 5.4 | 9.7 | 28 | 0.048 | +4.3 |
| 1651 | 22 | 3.1 | 9.9 | 30.4 | 0.048 | +4.1 |
| 1682 | 44 | 6.1 | 17 | 49.5 | 0.048 | +4.2 |
| 1693 | 40.5 | 3.4 | 24 | 69 | 0.029 | +5.9 |
|  |  |  |  |  | Avg. | +5.2 |

## Table II

### Ion Intensities, Equilibrium Constants and Third-Law
### Heats for the Reaction
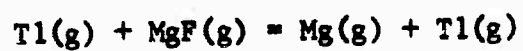
$$Tl(g) + MgF(g) = Mg(g) + TlF(g) \qquad (2)$$

| $T(^\circ K)$ | $I(Tl^+)$ 12 V. | $I(TlF^+)$ 17 V. | $I(Mg^+)$ 13 V. | $I(MgF^+)$ 13 V. | $K_2$ | $\Delta H_{298}(2)$ Kcal/mole |
|---|---|---|---|---|---|---|
| 1546 | 560 | 2 | 380 | 20 | 0.068 | +5.3 |
| 1573 | 967 | 3.5 | 700 | 43 | 0.059 | +5.8 |
| 1579 | 700 | 2.5 | 520 | 33 | 0.056 | +6.0 |
| 1585 | 867 | 5 | 733 | 50 | | +4.8 |
| | | | | | Avg. | +5.5 |

## Table III

Comparison of Bond Dissociation Energies of Group IIIA Monofluorides
as Obtained from Spectroscopic and from Thermochemical Studies

| | $D_o''$ (Thermochemical) Kcal/mole | $D_o''$ (Spectroscopic) from $^1\Pi$ State Kcal/mole | Difference Kcal/mole |
|------|------|------|------|
| BF | 180 | 185 | 5 |
| AlF | 159 | 167 | 8 |
| GaF | 138 | 144 | 6 |
| InF | 121 | 126 | 5 |
| TlF | 101.4 | 109.5* | 8 |

\* $^1\Pi$ state for TlF gives a continuum. Value given is from $^3\Pi$ state.
Barrow has pointed out that if there is a maximum in the $^3\Pi$ state,
one would expect a similar maximum in the $^1\Pi$ state.